

Retarded and nonretarded van der Waals interactions between a cluster and a second cluster or a conducting surface

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Abstract

In some respects, a cluster consisting of many atoms may be regarded as a single large atom. Knowing the dielectric properties of such a cluster permits one to evaluate the form of the van der Waals (dispersion) interactions between two clusters or between one cluster and a surface. In this paper, we derive these interactions in two extreme opposite regimes of separation: fully retarded and nonretarded. In the fully retarded regime (very large separation), the magnitude of the interaction is determined by just the *static* polarizability of the cluster(s). In the nonretarded regime (small separation), we employ a single resonant frequency model of the cluster polarizability to derive expressions for the interactions' coefficients. Numerical examples are presented to demonstrate that many-body screening of these interactions can be significant. The results represent the corrections to the commonly used approximation of pairwise additivity of interatomic interactions.

I. INTRODUCTION

Van der Waals (vdw) interactions have been much studied in recent years, in part because of increasing interest in phenomena involving surfaces, interfaces, and nanoparticle interactions^{1,2,3,4,5,6,7}. In this paper, we evaluate two distinct interactions involving clusters, which we assume to be spherical. One of these is the interaction between two clusters, denoted A and B; the other is the interaction between a cluster and a flat surface. We consider both of these interactions in two extreme opposite regimes of separation: *nonretarded* and *fully retarded*, corresponding to small separation and very large separation, respectively. The word “small” is used advisedly because we assume throughout this paper that the separation is large compared to the size of the clusters.

Nonretarded vdw interactions, sometimes called *London forces*, can be derived from quantum mechanics and electrodynamics. Most research involving interactions within condensed states of matter pertains to the nonretarded regime because short-range forces predominate in determining the physical behavior of such systems. However, the onset of effects of retardation occurs at sufficiently small distance scales (≈ 10 nm) that such effects are often present to some extent; they become particularly important when studying large molecules or clusters, because of their size. The interaction is said to be *fully retarded*^{8,9,10} in the separation regime where the finite speed of light causes a significant attenuation of the (nonretarded) vdw interaction. Indeed, even the power law describing the distance dependence of the interaction is altered by retardation (increasing the falloff by one power of distance). The regime of retardation is that where the separation r is large compared to both the cluster size (radius R) and a *typical* wavelength λ determined by the spectra of both interacting species: $\lambda = hc/\Delta E$; here ΔE is a characteristic energy in the electronic spectrum of the cluster and/or surface. If ΔE is the first ionization energy, for example, then $\lambda \approx 0.1$ to 1 micron (for Na and Si, $\lambda \approx 0.24$ microns and 0.15 microns, respectively). The surface force apparatus has been used to measure van der Waals forces between two macroscopic mica surfaces¹¹. Other techniques (e.g., atomic force microscopy¹² and total internal reflection microscopy¹³ have been used to measure interaction forces, and a few techniques (e.g., laser trapping¹⁴ and differential electrophoresis¹⁵) have been used to measure sub-piconewton interaction forces between Brownian particles. Figure 1 presents results for the interaction between two Na clusters obtained in this paper for the nonretarded and fully

retarded regimes, along with a plausible interpolation over the interval $0.1 < r/\lambda < 10$.

Because vdw interactions arise from fluctuating electromagnetic fields in the interacting media, there arise many-body effects associated with screening of these interactions by neighboring particles within a cluster. This means that one should not simply add together the interactions of individual particles without taking the screening into account¹⁶. As an example, we demonstrate the importance of screening in the case of alkali metal clusters. There occurs a general increase in the effect of screening as a function of cluster size, but the trend is not completely monotonic because of electronic shell effects on the cluster's polarizability.

The outline of this paper is the following. Section II describes the case of fully retarded interactions. In that case, the vdw interaction is determined by just the static polarizability of the interacting clusters (because long wavelength fields give rise to the interaction). In Section III, we explore the nonretarded regime, for which all wavelengths contribute, in principle. That treatment requires the introduction of a model form for the polarizability as a function of frequency. In the present case, we employ the simplest possible model (single resonant frequency) that is consistent with both the static value and the known high frequency limit of the polarizability. Section IV summarizes our results and comments about possible extensions to related problems.

II. FULLY RETARDED REGIME

The starting point of our analysis is the fact that the fully retarded interaction between two atoms (here denoted a and b) separated by distance r (with $r \gg \lambda$) is known to satisfy⁸:

$$V_{ab}(r) = -K \frac{P_a^0 P_b^0}{r^7} \quad , \quad K = \frac{23hc}{8\pi^2} \quad (1)$$

Note the interesting fact that the interaction falls off with distance as r^{-7} , with a coefficient determined by the *static* atomic polarizabilities (P_a^0 , P_b^0) of the species involved. This behavior contrasts with the nonretarded vdw interaction in both the latter's power law (r^{-6}) and its dependence on the frequency-dependent polarizability, rather than just the static value P^0 (see Eqs. 10 and 11 below).

A. Cluster-cluster interaction

We now turn to the problem of the interaction between two clusters. The key idea of this paper is simple: one may treat a cluster as though it is a large atom, insofar as the cluster has an excitation spectrum with an energy gap and it is of finite extent. Here, we consider the case of separation r large compared to its size. Specifically, the present calculation requires that the cluster's radius $R \ll \lambda \ll r$. Validity of that criterion permits one to use the local, dipolar approximation to describe the electrodynamic response of the cluster to the fluctuating electromagnetic fields that are responsible for vdw interactions. Based on this argument, the interaction between two clusters A and B may be written

$$V_{AB}(r) = -K \frac{P_A^0 P_B^0}{r^7} \quad (2)$$

Here P_A^0 and P_B^0 are the static polarizability of cluster A and B, respectively, a subject of much attention in recent years^{17,18,19,21}. Now, one may ask a simple question: how different is this cluster-cluster interaction from a naive estimate, V_{est} , obtained from summing pairs of interactions between the constituent a, b atoms? The latter may be written as a product of the interatomic pair interaction and the number of such interactions between the two clusters:

$$V_{est}(r) = N_A N_B V_{ab}(r) = -K N_A N_B \frac{P_a^0 P_b^0}{r^7} \quad (3)$$

We compute the ratio of the exact result Eq. (2) to this estimate and define the ratio as a “screening” function S_{AB}^r :

$$S_{AB}^r(r) = \frac{V_{AB}(r)}{V_{est}(r)} = \frac{P_A^0(N_A)}{N_A P_a^0} \frac{P_B^0(N_B)}{N_B P_b^0} = f_A(N_A) f_B(N_B) \quad (4)$$

This screening function is separable, a product of two independent screening functions $f(N)$, each of which is the ratio of the cluster's polarizability to a nominal cluster polarizability, equal to the product of the atomic polarizability and the number of atoms. Because each of these f functions is less than one if $N > 1$, then $S_{AB}^r < 1$ if either of the clusters possesses more than one atom. Thus the true interaction is reduced relative to the naive estimate V_{est} .

Figure 2 presents the screening function for the case of a Na cluster interacting with a second Na cluster. The static polarizability of the Na clusters $P^0(N)$ was taken from

theoretical results, obtained using the jellium model and density-functional calculations¹⁸. This simple model was adequate to explain the experimental polarizability data¹⁹. For the extreme case $N_A = 1 = N_B$, the screening function is unity, by definition. For increasing N , typically, the screening causes S_{AB}^r to decrease below one. Note that the reduction is by a factor near 0.4 for two 40 atom Na clusters and this is essentially the asymptotic value²⁰ for $N_A, N_B \rightarrow \infty$. The dependence on number is not monotonic, however, because of shell structure of the electronic states of the cluster. This nonmonotonic behavior makes the figure interesting; notice the shape of a “bat head” in the center of the Figure 2.

We remark that the hypothetical case of clusters comprised of weakly polarizable, inert gases represents an instance for which the functions whose product determines S_{AB}^r are close to 1, i.e. $P_A^0 = N_A P_a^0$. Indeed, in the framework of local, continuum electrostatics, this relation is exact if the Clausius-Mossotti relation describes the static dielectric constant ϵ of the material, since the dipole moment of a dielectric cluster²² in an external field \mathbf{E} is $[(\epsilon - 1)/(\epsilon + 2)]R^3\mathbf{E}$. Thus, the interaction between two such inert gas clusters is *not* significantly screened.

B. Cluster-surface interaction

Next, we address very briefly the case of a cluster (A) near the surface of a semi-infinite perfectly conducting metal, a simplified version of a more general adsorption problem. In that case, the cluster’s interaction with the surface obeys a relation³

$$V_{cond} = -K' \frac{P_A^0}{z^4} \quad (5)$$

Here $K' = 3hc/(16\pi^2)$ and z is the separation between the cluster’s center and the boundary of the surface. The ratio of this cluster-surface interaction to a naive estimate, based on N_A individual constituent atoms of the cluster is analogous to the ratio S_{AB}^r for the cluster-cluster interaction:

$$\frac{V_{cond}}{V_{est}} = \frac{P_A^0(N_A)}{N_A P_a^0} = f_A(N_A) \quad (6)$$

This behavior therefore involves the same function as the previous problem²³.

Finally, we evaluate the retarded cluster-surface interaction in the case of a solid made of molecules of static polarizability P_m^0 and density n . We specialize the discussion to the

situation where the product $nP_m^0 \ll 1$; this weak-screening limit is essentially the extreme opposite case from the perfect conductor considered above. In this new limit, the interaction V_{weak} can be evaluated by integrating the cluster-molecule interaction density $-KnP_A^0P_m^0/r^7$ over the half-space $z < 0$ in the presence of the cluster, centered at distance d above the surface:

$$V_{weak}(d) = -nKP_A^0P_m^0 \int_{z' < 0} \frac{d\mathbf{r}'}{|\hat{\mathbf{z}}d - \mathbf{r}'|^7} \quad (7)$$

The result of that integration is:

$$V_{weak}(d) = -\frac{\pi}{10}Kn\frac{P_A^0P_m^0}{d^4} = -\frac{23}{80\pi}\frac{\hbar c n P_m^0P_A^0}{d^4} \quad (8)$$

We may compute the ratio of this interaction to that of the perfect conductor with the same cluster (Eq. (5)):

$$\frac{V_{weak}}{V_{cond}} = \frac{23}{15}\pi nP_m^0 \quad (9)$$

Note that these interactions strengths are similar if $nP_m^0 \approx 0.2$. Even for such a small polarizability, therefore, the interaction is comparable to that obtained with a perfect conductor. In the case of an Ar solid, in contrast, the ratio in Eq. (9) is about 0.2.

III. NONRETARDED INTERACTION

We first recall that the nonretarded interaction between two atoms a and b separated by a distance r is given by⁸

$$V_{ab}(r) = -\frac{C_6^{ab}}{r^6} \quad (10)$$

where the constant C_6^{ab} is

$$C_6^{ab} = \frac{3\hbar}{\pi} \int_0^\infty du P_a(iu) P_b(iu) \quad (11)$$

Here, $P_a(\omega)$ and $P_b(\omega)$ are the dynamic polarizabilities of the atoms, continued to imaginary frequencies $\omega = iu$. The atomic polarizability has the form

$$P_a(iu) = \frac{e^2}{m} \sum_n \frac{f_{0n}}{\omega_{0n}^2 + u^2} \quad (12)$$

where f_{0n} is the oscillator strength that measures the probability of the transition from the ground state 0 to the excited state n , at frequency ω_{0n} .

A. Cluster-cluster interaction

To compute the interaction between two clusters A and B, we use the same idea as in the last section of considering the clusters as large atoms ($R \ll r \ll \lambda$). In that case, we may write the cluster-cluster interaction as:

$$V_{AB}^{nr}(r) = -\frac{C_6^{AB}}{r^6} \quad , \quad C_6^{AB} = \frac{3\hbar}{\pi} \int_0^\infty du P_A(iu) P_B(iu) \quad (13)$$

We propose a simple form for the dynamical polarizability of the cluster²⁴:

$$P_A(iu) = \frac{P_A^0}{1 + \frac{u^2}{\omega_A^2}} \quad (14)$$

designed to give the static polarizability of the cluster at zero frequency, and the known asymptotic behavior, $P_A \rightarrow ZN_A e^2 / (mu^2)$ in the high frequency limit (free electrons) if we define ω_A with

$$\omega_A^2 \equiv \frac{ZN_A e^2}{mP_A^0} \quad (15)$$

Here m is the electron mass and Z is the number of electrons in the atom. An analogous approximation can be made for the atomic polarizability $P_a(iu)$ using a single characteristic frequency ω_a to determine its form. The characteristic frequency of the cluster, ω_A , is larger than the corresponding result for a single atom, ω_a , by a factor of $1/\sqrt{f_A}$. We have tested the quality of our proposed function by comparing it with the dynamical polarizability of small metal clusters, calculated by Kresin within the random-phase approximation²¹. He finds two collective excitations (one surface mode and one volume mode) in terms of which he evaluates the dynamical polarizability. We have found that the overall frequency dependences of his expression and Eq. (14) agree very well, with a difference less than 0.5 %.

Assuming the cluster polarizability to be that from Eq. (14) (and using the corresponding approximation for the atomic polarizability), we compute the ratio S_{AB}^{nr} between the nonretarded cluster-cluster interaction and the simple estimate that results from summing pair interactions, assuming $Z = 1$:

$$S_{AB}^{nr} = \frac{C_6^{AB}}{N_A N_B C_6^{ab}} = \frac{\omega_a \omega_b (\omega_a + \omega_b)}{\omega_A \omega_B (\omega_A + \omega_B)} = \sqrt{f_A f_B} \frac{(P_a^0)^{-1/2} + (P_b^0)^{-1/2}}{(f_A P_a^0)^{-1/2} + (f_B P_b^0)^{-1/2}} \quad (16)$$

Figure 3 shows this function for the case of two interacting Na clusters. It shares the same qualitative behavior as the screening function in the retarded case (Eq. (4)). In the case $a = b$, $N_A = N_B$, $S_{AB}^{nr} = f_A^{3/2}(N_A)$. This compares with the result f_A^2 in the fully retarded limit (Eq. (4)).

B. Cluster-surface interaction

The nonretarded vdw interaction between an atom and a surface at separation d is given by³

$$V_{a-surf}(r) = -\frac{C_3^{a-surf}}{d^3} \quad (17)$$

with

$$C_3^{a-surf} = \frac{\hbar}{4\pi} \int_0^\infty du P_a(iu) g(iu) \quad (18)$$

Here, $g(iu)$ is the dielectric response function of the substrate

$$g(iu) = \frac{\epsilon(iu) - 1}{\epsilon(iu) + 1} \quad (19)$$

which can be approximated by

$$g(iu) = \frac{g_0}{1 + \frac{u^2}{\omega_s^2}} \quad (20)$$

if the response is dominated mainly by the resonance at ω_s (the surface plasmon resonance in the case of a metal). The parameter g_0 is equal to 1 in the case of a free electron metal, in which case the ansatz Eq. (20) is exact, with $\omega_s = \sqrt{2}$ times the bulk plasma frequency. Following the spirit of the previous sections, the van der Waals coefficient for the cluster-surface problem is

$$\frac{C_3^{A-surf}}{N_A} = \frac{\hbar}{4\pi} \int_0^\infty du \frac{P_A(iu)}{N_A} g(iu) = \frac{g_0 f_A P_a^0}{8} \frac{\hbar \omega_s}{\left(1 + \frac{\omega_s}{\omega_a}\right)} \quad (21)$$

After carrying out the integrations for C_3^{A-surf} and C_3^{a-surf} , the screening function for the cluster-surface interaction results:

$$S_{A-surf} = \frac{C_3^{A-surf}}{N_A C_3^{a-surf}} = f_A \frac{1 + \frac{\omega_s}{\omega_A}}{1 + \frac{\omega_s}{\omega_A} \sqrt{f_A}} \quad (22)$$

We plot this function in Figure 4, for different ratios ω_s/ω_A . As can be seen in the figure, $S_{A-surf} \rightarrow \sqrt{f_A}$, if $\omega_s \gg \omega_A$, and goes to f_A when $\omega_s \ll \omega_A$. This relative interaction ratio is the smallest in the latter case (since $f_A < 1$).

IV. SUMMARY

In this paper we have evaluated two kinds of interaction (cluster-cluster and cluster-surface) in two extreme opposite regimes of separation (nonretarded and fully retarded).

We have described a particularly simple result for the fully retarded interactions involving clusters. The interaction between two clusters is reduced (relative to the naive estimates) by a screening function, derived from the product of individual cluster screening functions $f(N)$, that depend on the electronic properties of the cluster. Because the latter shows interesting, nonmonotonic behavior as a function of atomic number, the dependence on the individual clusters' numbers is nontrivial, as exemplified in Figure 2. Qualitatively similar behavior occurs in the nonretarded case, seen in Figure 3.

This work can be generalized in many ways. One potential extension involves exploration of the intermediate regime of separation. While straightforward in principle, this is complicated in practice, so we simply mention results obtained elsewhere for analogous problems in this intermediate separation regime (the dashed region in Figure 1). In the case of the interaction between two identical atoms, the effect of retardation is to reduce the nonretarded interaction by a factor of two when the atoms are separated by one-tenth of the characteristic wavelength in their excitation spectrum (i.e., r is about 40 nm if the relevant energy is 3 eV²⁵). In the case of the interaction between an inert gas atom, or small molecule, and a surface, the corresponding distance is somewhat smaller, about 20 nm²⁶. These distances are sufficiently small that one should not ignore the effects of retardation in many applications. If one were to accept the linear interpolation in Figure 1, the ratio of this interaction to the (extrapolated) nonretarded interaction at $r = \lambda$ would be 0.49.

The second problem of potential interest is the effect of a medium in which the clusters are dissolved. This is the principal focus of our future research. A third problem of potential interest is larger clusters (i.e. radii *not* much smaller than their separation). Both of these present no question of principle but neither problem is as simple computationally as the problems described here.

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- ¹ M.J. Elrod and R.J. Saykally, Chem. Rev. **94**, 1975 (1994).
 - ² A.D. Buckingham, P.W. Fowler and J.M. Hutson, Chem. Rev. **88**, 963 (1988).
 - ³ L.W. Bruch, M.W. Cole and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Oxford, 1997).
 - ⁴ M. Schmeits and A.A. Lucas, Prog. Surf. Sci. **14**, 1 (1983).
 - ⁵ J.N. Israelachvili, *Intermolecular and surface forces*. Academic Press, London (1992).
 - ⁶ S.R. Nicewarner-Pena, R.G. Freeman, B.D. Reiss, L. He, D.J. Pena, I.D. Walton, R. Cromer, C.D. Keating, M.J. Natan, Science **294**, 137 (2001).
 - ⁷ P.C. Zamora and C.F. Zukoski, Langmuir **12**, 3541 (1996).
 - ⁸ H. Margeneau and N.R. Kestner, *Theory of Intermolecular Forces*, (2nd edn). Pergamon, Oxford (1971).
 - ⁹ H.B.G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).
 - ¹⁰ I.E. Dzyaloshinskii, E.M. Lifshitz, and L.P. Pitaevskii, Advances in Physics **10**, 165 (1961).
 - ¹¹ J.N. Israelachvili and G.E. Adams, J. Chem. Faraday Trans. **74**, 975 (1978).
 - ¹² W.A. Ducker, T.J. Senden, R.M. Pashley, Nature **353**, 239 (1991).
 - ¹³ D.C. Prieve, F. Luo, F. Lanni, Faraday Disc. Chem. Soc. **83**, 297 (1987); D.C. Prieve, N.A. Frej, Faraday Disc. Chem. Soc. **90**, 209 (1990).
 - ¹⁴ J.C. Crocker, J.A. Matteo, A.D. Dinsmore, A.G. Yodh, Phys. Rev. Lett. **82**, 4352 (1999).

- ¹⁵ D. Velegol, J.L. Anderson, S. Garoff, *Langmuir* **12**, 4103 (1996); J.L. Anderson, D. Velegol, S. Garoff, *Langmuir* **16**, 3372 (2000).
- ¹⁶ H.C. Hamaker, *Physica* **4**, 1058 (1937).
- ¹⁷ W.A. de Heer, *Rev. Mod. Phys.* **65**, 611-676 (1993); M. Brack, *Rev. Mod. Phys.* **65**, 677 (1993).
- ¹⁸ M. Manninen, R.M. Nieminen, and M.J. Puska, *Phys. Rev. B* **33**, 4289 (1986).
- ¹⁹ W.D. Knight, K. Clemenger, W.A. de Heer, and W.A. Saunders, *Phys. Rev. B* **31**, 2539 (1985).
- ²⁰ This asymptotic value is a consequence of the behavior of the individual screening functions $f(N)$ for large N , that decrease from unity for $N=1$ until they reach an approximately constant value $f(N) \approx 0.6$ for $20 < N < 40$.
- ²¹ V. Kresin, *Phys. Rev. B* **42**, 3247 (1990).
- ²² J.D. Jackson, *Classical Electrodynamics* (2nd edn). J. Wiley and Sons, New York (1975).
- ²³ We note that G.L. Klimchitskaya, U. Mohideen and V.M. Mostepanenko (*Phys. Rev. A* **61**, 062107, 2000) have derived a different expression for a related quantity. Their result is determined for the case when R greatly exceeds the distance to the surface, which itself is diverging. The present case involves finite R , which is assumed to be much smaller than the distance z .
- ²⁴ Such a single frequency approximation has been widely used in computing interatomic interactions and adsorption interactions (see Refs. 3, 4 and 5).
- ²⁵ See Ref. 8, p.236.
- ²⁶ E. Cheng and M.W. Cole, *Phys. Rev. B* **38**, 987 (1988).

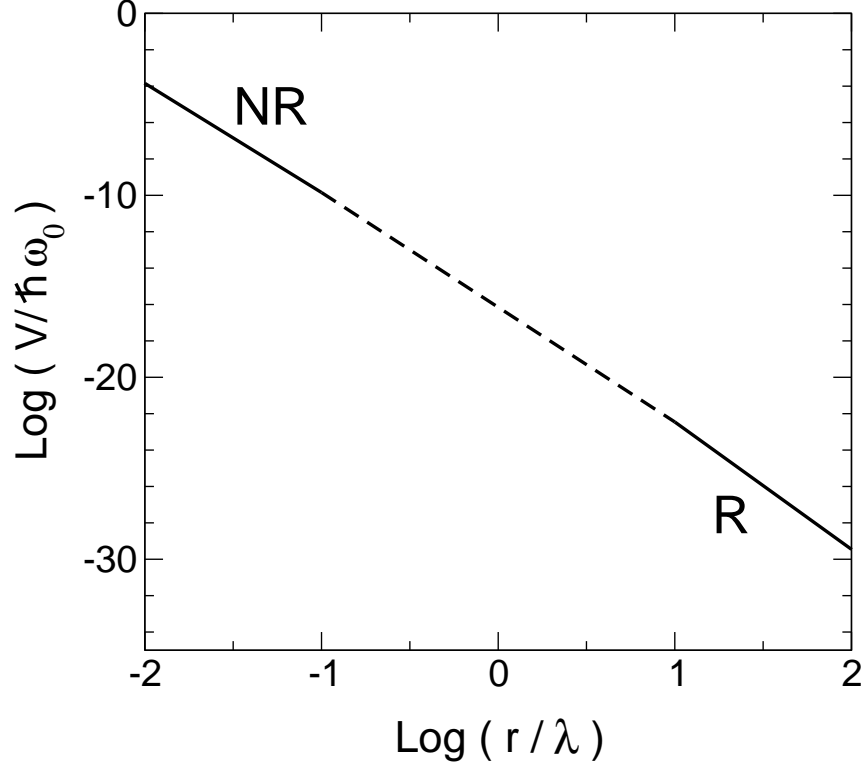


FIG. 1: Different regimes of the van der Waals interaction between two 20 Na atoms clusters, in units of a characteristic energy $\Delta E = \hbar\omega_0$. The nonretarded regime (NR) when $R/\lambda \ll r/\lambda \ll 1$ is analyzed in Section III, and the retarded regime for separations such that $r/\lambda \gg 1 \gg R/\lambda$ is explored in Section II. The intermediate regime (dashed line) is not considered in this work, but note that it can be interpolated between the r^{-6} (nonretarded) and r^{-7} (retarded) functional forms.

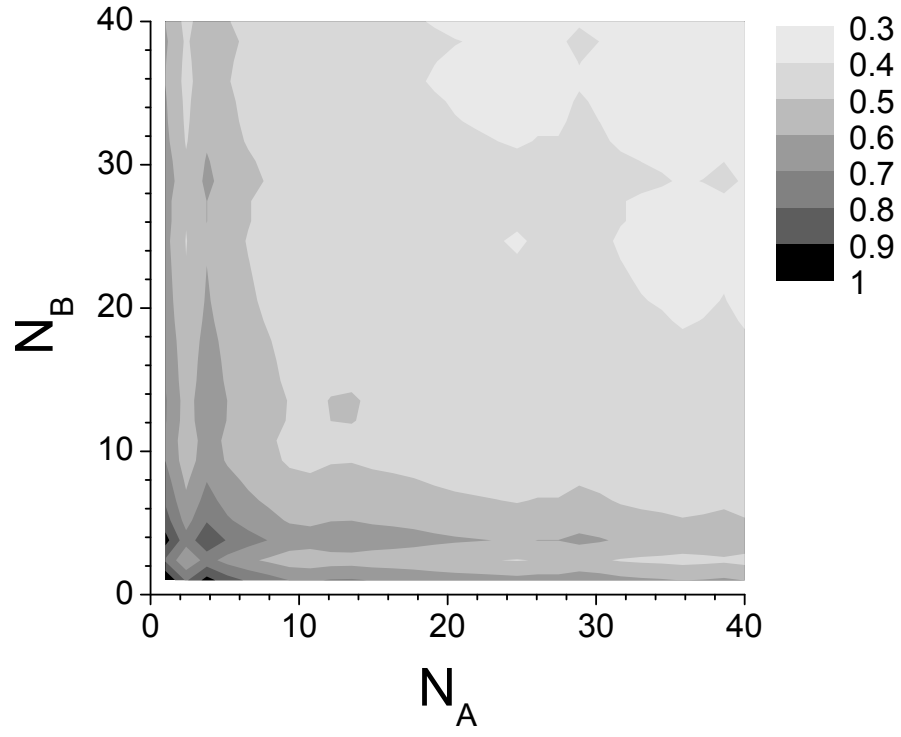


FIG. 2: Retarded screening function $S^r(N_A, N_B)$ for the case of two Na clusters containing N_A and N_B atoms, respectively.

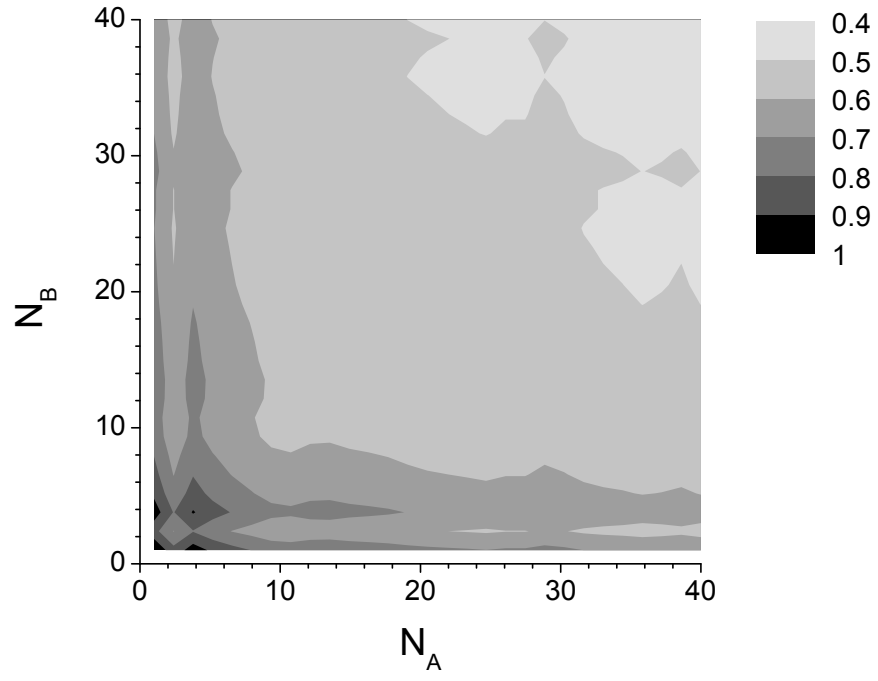


FIG. 3: Same as Fig. 1 for the nonretarded interaction.

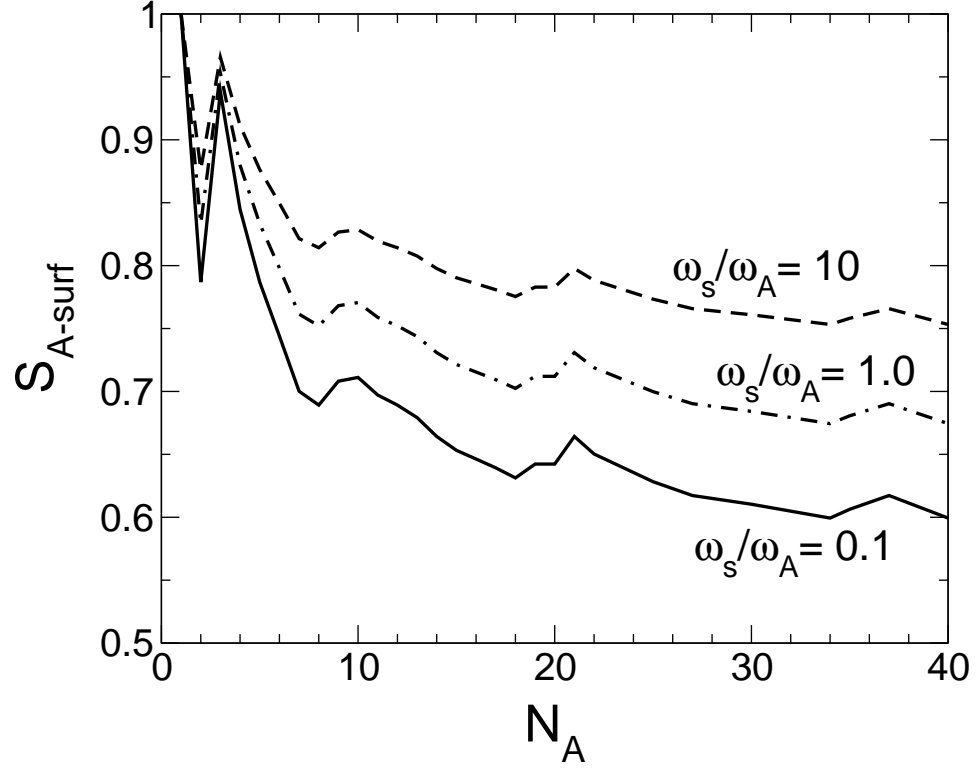


FIG. 4: Nonretarded screening function S_{A-surf} for the case of a Na cluster of N_A atoms interacting with a surface which has a characteristic energy $\hbar\omega_s$.